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QUANTITATIVE CONFIRMATION OF DIFFUSION-LIMITED OXIDATION THEORIES. K. T. Gillen and R. L. Clough, Sandia National Laboratories, Albuquerque, NM 87185

Diffusion-limited (heterogeneous) oxidation effects are often important for studies of polymer degradation. Such effects are common in polymers subjected to ionizing radiation at relatively high dose rate. To better understand the underlying oxidation processes and to aid in the planning of accelerated aging studies, it would be desirable to be able to monitor and quantitatively understand these effects. In this paper, we briefly review a theoretical diffusion approach which derives model profiles for oxygen-surrounded sheets of material by combining oxygen permeation rates with kinetically based oxygen consumption expressions. The theory leads to a simple governing expression involving the oxygen consumption and permeation rates together with two model parameters α and β. To test the theory, gamma-initiated oxidation of a sheet of commercially formulated EPDM rubber was performed under conditions which led to diffusion-limited oxidation. Profile shapes from the theoretical treatments are shown to accurately fit experimentally derived oxidation profiles. In addition, direct measurements on the same EPDM material of the oxygen consumption and permeation rates, together with values of α and β derived from the fitting procedure, allow us to quantitatively confirm for the first time the governing theoretical relationship.

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QUANTITATIVE CONFIRMATION OF DIFFUSION-LIMITED OXIDATION THEORIES

by

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INTRODUCTION

Exposure of polymers to air during aging (radiation, thermal, UV) often results in inhomogeneously oxidized samples, a complication which impacts attempts both to understand the oxidation process and to extrapolate accelerated exposures to long-term conditions. The most important such complication involves diffusion-limited oxidation which can occur if the rate of oxygen consumption in a material is greater than the rate at which oxygen can be resupplied by diffusion processes from the surrounding air atmosphere. This will usually lead to a heterogeneity in the oxidation across the material, with equilibrium oxidation (e.g., corresponding to air-saturated conditions) occurring at the sample surfaces and reduced or non-existent oxidation in the interior. The importance of this effect will depend on material geometry coupled with oxygen consumption and permeation rates. [1,2] Frequently, the percentage of the sample which is oxidized under accelerated (higher-level) environmental conditions is substantially lower than the percentage oxidized under lower-level, application conditions. [2-8] Thus, in order to confidently extrapolate accelerated simulations to long-term, air-aging conditions, one must be able to monitor and quantitatively understand diffusion-limited oxidation effects. Experimental techniques for monitoring diffusion-limited oxidation profiles have recently been reviewed. [2-11] By comparing experimental profiles with theoretically derived profiles, the theories can be verified and then confidently used to predict the importance of diffusion effects prior to the initiation of aging tests. This paper summarizes what we believe is the first quantitative experimental confirmation of diffusion-limited oxidation theories.

DIFFUSION-LIMITED OXIDATION THEORIES

In order to quantitatively model diffusion-limited oxidation profiles, one must combine expressions for oxygen consumption with diffusion equations. To derive oxygen consumption rates, detailed knowledge of the kinetics of oxidation must exist, a difficult requirement given the complexities of oxidation processes in polymers. [12] Most modelling attempts assume that the scheme shown in Fig.1 [13,14] represents a rea- sonable first order approximation for the oxidation of organic materials in various environments (thermal, mechanical, UV light, ionizing radiation, etc.). Environmental differences occur mainly in the details of the free-radical producing initiation step. It is often easiest to control the initiation rate in the gamma-initiated case, since R_i is typically independent of aging time and linear with the radiation dose rate. In addition, branching reactions, which may enter and complicate the oxidation processes occurring at the high temperatures used for thermal oxidation studies, are often unimportant for lower temperature, gamma-initiated oxidation. Any growth in importance of branching reactions as degradation proceeds will cause the oxidation rate to increase with time, further complicating attempts at quantitative modelling. For these reasons, gamma-initiated oxidation is the best choice for initial attempts at quantitatively modelling diffusion-limited oxidation effects. Complications, such as time-dependent oxidation rates, may then be addressed once confidence exists in models derived for the simpler situations.

For gamma-initiated oxidations involving moderate temperatures, we will therefore assume that the chemistry is adequately represented by rxs. (1)- (8) in Fig. 1. The scheme involving the bimolecular termination steps (rxs. (1)- (6)), originally derived for the oxidation of organic liquids, has been invoked for many years for explaining the oxidation of polymers. Using a steady-state analysis and assuming long kinetic chain lengths (many propagation cycles compared to termination reactions) and $k_5^2 = 4k_4k_6$, the oxygen consumption rate is given by [13]

$$\frac{dO_2}{dt} = \frac{C_1\ [O_2]}{1 + C_2[O_2]} \qquad (1)$$

where the constant $C_1 = k_2R_i^{0.5}/(2k_4)^{0.5}$ and the constant $C_2 = (k_6/k_4)^{0.5}k_2/k_3$ and $k_3 = k_3'[RH]$.

For many polymeric materials, unimolecular termination reactions are often found to be dominant. For instance, in the presence of sufficient antioxidant, the radical species ($RO_2\cdot$ and $R\cdot$) can terminate in pseudo first-order reactions, yielding an oxidation scheme consisting of rxs. (1)- (3) plus (7) and (8). The rate of oxidation is then given by an expression identical in form to eq. (1), except that $C_1 = (k_2/k_8)R_i$ and $C_2 = (k_2/k_8)k_7/(k_3+k_7)$. [2] Although the bimolecular and unimolecular schemes yield oxygen consumption rates that have identical functional dependencies on the oxygen concentration, their dependencies on the initiation rate, R_i, are quite different (half- and first-order, respectively). Thus, if data at various initiation rates were available, one could distinguish between the two schemes.

By combining the bimolecular kinetic scheme result with diffusion expressions, and assuming that the oxygen consumption and permeation rates are independent of time, Cunliffe and Davis [1] derived theoretical oxidation profiles for slabs of material of thickness L. Their steady-state results depended on two parameters, α and β, given by

$$\alpha = C_1L^2/D \quad \text{and} \quad \beta = C_2Sp = C_2[O_2]_e \qquad (2)$$

where D and S are the diffusion and solubility parameters in the material, p is the oxygen partial pressure of the surrounding atmosphere and $[O_2]_e$ denotes the dissolved oxygen concentration at the edge of the sample. Figure 2 shows the resulting theoretical profiles of normalized oxidation, and the corresponding steady-state oxygen concentration, for a sheet of material exposed on both sides to oxygen. [2] P gives the percentage of the distance from one oxygen-exposed surface of the sheet to the opposite oxygen-exposed surface. Since the profiles are symmetric, results are only shown for P ranging from 0 to 50%. For small values of β, the oxidation is proportional to the oxygen concentration, yielding "U-shaped" profiles. When β is large, oxidation is insensitive to oxygen concentration until the latter has dropped significantly, resulting in "step-shaped" profiles. For intermediate values of β, profile shapes of intermediate character result. If experimental data can be used to generate values of α and β, the following theoretical relationship [1] can be tested

$$R_oL^2/(pP_{ox}) = \alpha/(\beta + 1) \qquad (3)$$

where R_o represents the equilibrium oxygen consumption rate and P_{ox} is the oxygen permeation rate through the material. Since the unimolecular scheme results in an identical dependence of oxygen consumption on oxygen concentration, the same theoretical profiles are valid [2] except for the differing values of C_1 and C_2 as noted above.

QUANTITATIVE TEST OF THEORETICAL OXIDATION PROFILES

The above theory will now be quantitatively tested. Only a brief summary of the results is included here; a more complete discussion will be published shortly. [15] Since the theory was derived assuming steady-state conditions, a successful validation requires a system in which R_o and P_{ox} are relatively constant with aging time. In contrast to thermal aging situations, [16] these conditions often hold in high energy radiation environments. For example, in gamma-initiated oxidations of commercial elastomers, R_o is often relatively constant up to moderate total doses. [3,8] In addition, P_{ox} seldom changes by more than 10-20% for doses of 0.5 MGy. [17] For these reasons, a commercial EPDM rubber (Parker E740) was obtained in two thicknesses (3.02 mm and 1.8 mm) and aged in air (p = 13.2 cmHg O_2 partial pressure) at 6.65 kGy/h and 70°C. Experiments using gas chromatography showed that the oxygen consumption rate (R_o) under these conditions was constant and equal to 5.8×10^{-10} moles O_2/Gy/cc up to approximately 0.35 MGy, after which it began to rise. Oxygen permeation measurements on the unaged material allowed us to estimate that at 70°C, P_{ox} was equal to $7.3\pm0.7\times10^{-9}$ ccSTP/cm/cmHg/s. Changes in P_{ox} should be minor (no more than a few percent) for doses up to 0.35 MGy. [17] Thus, up to the limit of where the theory would be expected to hold for this material (0.35 MGy), the left hand side of Eq.(16) gives

$$R_oL^2/(pP_{ox}) = 22.7 \pm 3 \qquad (4)$$

for the 3.02 mm thick sample.

For doses up to 0.35 MGy, density changes (predominantly caused by oxidation [6]) were readily measured. The density profile technique [6] was therefore applied to material samples of both thicknesses after a total dose of 0.32 MGy. The resulting profiles of density changes caused by oxidation are plotted as crosses in Fig. 3; the vertical span represents the estimated experimental uncertainty with the horizontal span denoting the position and thickness of each slice. The best theoretical fits to this data occur for $\beta = 6$, together with $\alpha = 154.5$ (3.02 mm thick sample) and $\alpha = 55$ (1.8 mm thick sample). These calculated profiles are shown as the solid curves in Fig. 3. Note that this is a two-parameter fit since the two values of α must be related by the ratio of the squares of the sample thicknesses, as seen from Eq. (2). The results show that the theory does an excellent job of characterizing the profile shapes and their dependence on L. In addition, the resulting values of α and β from the fitting procedure yield

$$\alpha/(\beta + 1) = 22.1 \qquad (5)$$

for the thick sample. Since this independently calculated result is equal to the result found above in Eq. (4), the fit is consistent with the theoretical relationship given by Eq. (3), quantitatively verifying the theory.

As pointed out earlier, experiments as a function of initiation rate are necessary to choose between the two different kinetic schemes (bimolecular and unimolecular termination) underlying the theoretical profiles. The available evidence points to a linear dependence and would therefore seem to favor the unimolecular scheme. However, the real situation is far more complex and a complete discussion will appear in forthcoming presentations. [3,15]

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INITIATION	$\text{Polymer} \xrightarrow{R_i} R\cdot$	(1)
PROPAGATION	$R\cdot + O_2 \xrightarrow{k_2} RO_2\cdot$	(2)
	$RO_2\cdot + RH \xrightarrow{k_3'} ROOH + R\cdot$	(3)
BIMOLECULAR TERMINATION	$R\cdot + R\cdot \xrightarrow{k_4} \text{PRODUCTS}$	(4)
	$RO_2\cdot + R\cdot \xrightarrow{k_5} \text{PRODUCTS}$	(5)
	$RO_2\cdot + RO_2\cdot \xrightarrow{k_6} \text{PRODUCTS} + O_2$	(6)
UNIMOLECULAR TERMINATION	$RO_2\cdot \xrightarrow{k_7} \text{PRODUCTS}$	(7)
	$R\cdot \xrightarrow{k_8} \text{PRODUCTS}$	(8)
BRANCHING	$ROOH \xrightarrow{k_9} RO\cdot + \cdot OH$	(9)

Fig. 1. Oxidation kinetics

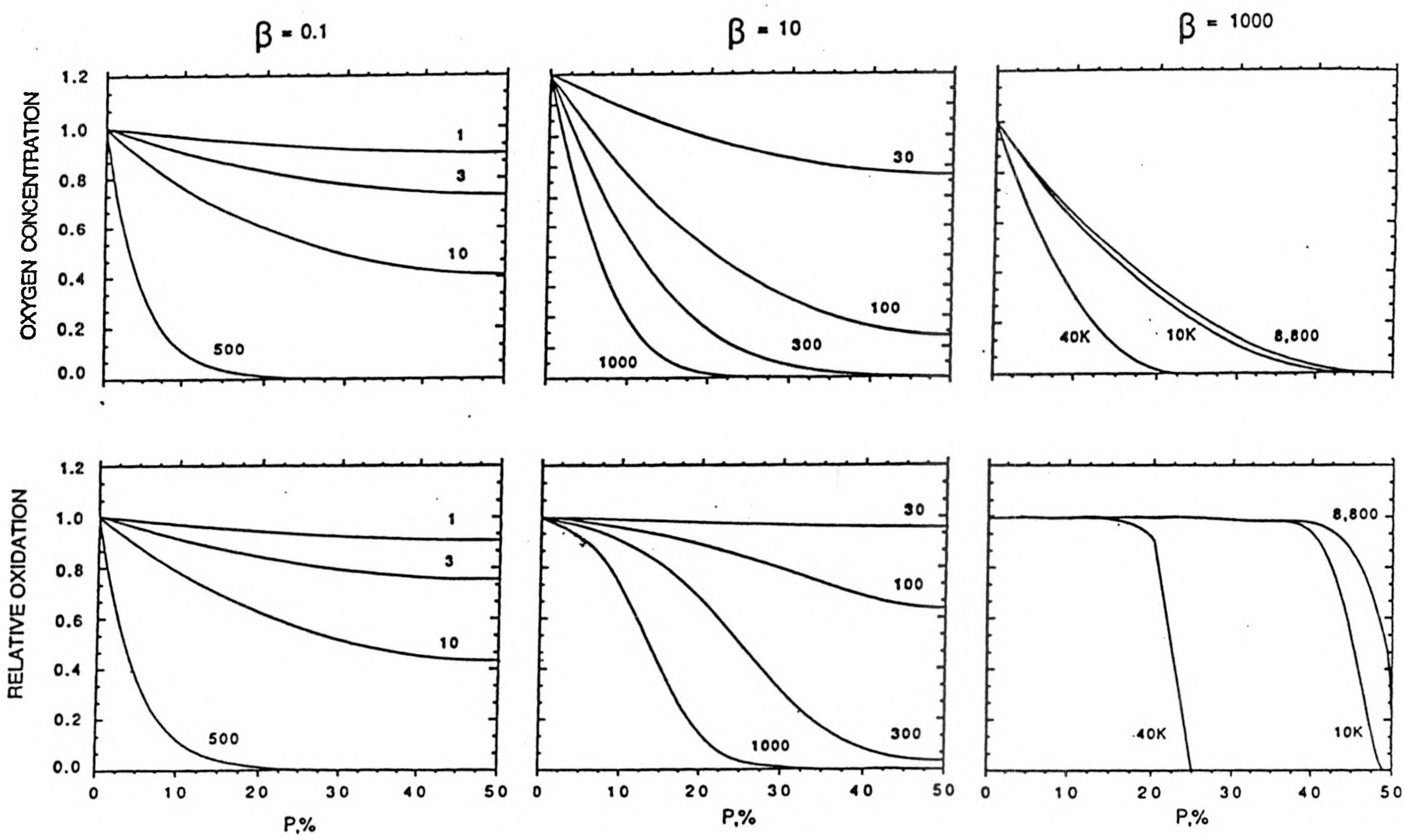

Fig. 2. Theoretical O_2 concentration (top) and corresponding oxidation (bottom) profiles at the three indicated β values (numbers on figures are selected values of α).

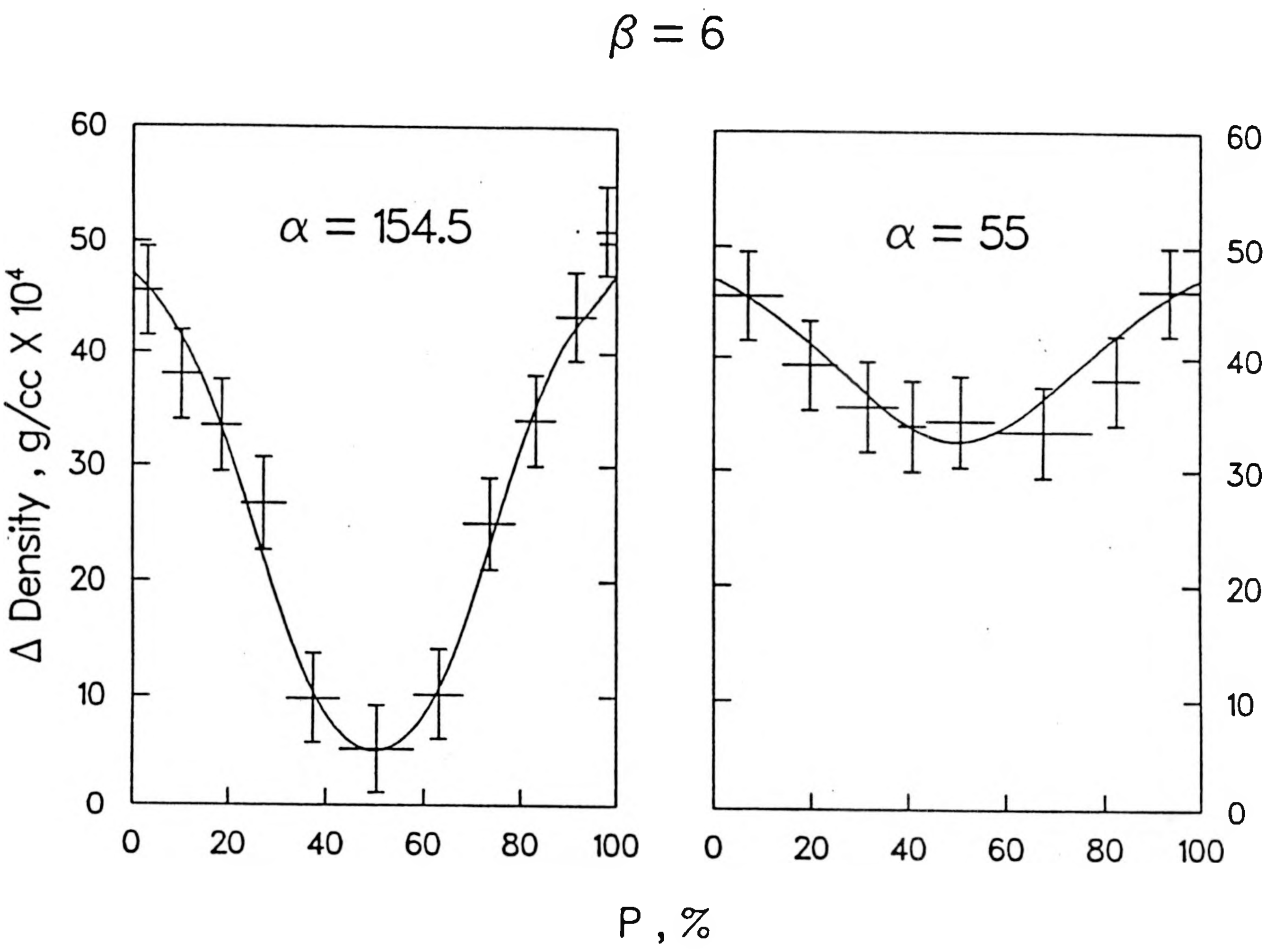

Fig. 3. Experimental profiles of density changes (crosses) for radiation aged 3.02 mm (left) and 1.8 mm (right) thick EPDM sheets. The curves through the data give the best theoretical fits using the parameters indicated.